Solvothermal conversion of technical lignins over NiMo catalysts

Ghafarnejad Parto, Soheila; Christensen, Jakob Munkholt; Pedersen, Lars Saaby; Taarning, Esben; Tjosås, Freddy ; Jensen, Anker Degn

Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

Solvothermal conversion of technical lignins over NiMo catalysts

Soheila G. Parto,[a] Jakob Munkholt Christensen,[a] Lars Saaby Pedersen,[b] Esben Taarning,[b] Freddy Tjosås,[c] Anker Degn Jensen [a,*]

[a]*Chemical Engineering, Technical University of Denmark, Kgs. Lyngby, 2800, Denmark*
[b]*Haldor Topsøe Company, Kgs. Lyngby, 2800 Denmark*
Borregaard Company, Sarpsborg, 1721, Norway

** Corresponding author: aj@kt.dtu.dk*

1. Scope

Lignin, cellulose and hemicellulose are the main constituents of plants cell walls. Lignin is an aromatic rich compound, composed of phenolic building blocks. Depending on the method used for isolation of lignin from cellulose and hemicellulose, several types of technical lignin are available such as Kraft lignin, Sulfonate lignin (Lignosulfonate), Soda lignin and Organosolv lignin. Despite being a natural aromatic compound, lignin is mainly treated as a low value by-product, and is burned for the energy supply of pulp and paper industries. By extraction of higher value products from lignin, a renewable source of valuable chemicals would be available and the economic viabilities of the relevant industries will be promoted. Most of the recent publications have targeted one type of lignin such as Kraft lignin [1]. However, it is desirable to introduce a method suitable for conversion of the range of available technical lignins. In this work, catalytic conversion of different types of lignin using an alumina supported NiMo catalyst (provided by Haldor Topsøe A/S) is conducted in ethanol at 310 ˚C with initial hydrogen pressure of 25 barg. The reaction time was set to 3 hours. Proton-Lignosulfonate (H-LS, provided by Borregaard A/S in form of Sodium-Lignosulfonate), Kraft lignin, Protobind 1000 and Organosolv lignin are among the selected lignin types. Non-catalytic conversion of each type of lignin was also performed at similar reaction conditions for comparison. The catalyst: lignin: solvent ratio of 1 g: 10 g: 100 ml was selected. The NiMo catalyst is a sulfur tolerant catalyst, which is originally present in the oxide form. The NiMo catalyst was presulfided before use to form $NiMoS_2$. Presulfidation was conducted overnight by in-situ decomposition of 10 ml dimethyl disulfide and formation of H_2S.

After each standard test, the solid and liquid reaction products were separated by vacuum filtration. Furthermore, the light and heavy liquid products were separated by rotary evaporation at 35 ˚C and 5 mbar. While the light fraction was rich in ethanol, the remaining fraction was heavy oil, attributed as ‘bio-oil’. GC-MS-FID analysis was used for identification and quantification of the bio-oil and ethanol rich light fraction. The molecular weight of the oil fraction was determined by size exclusion chromatography (SEC). Elemental analysis (Eurovector EuroEA3000) was conducted for measuring the organic C, H, S, N and O contents of the oil and solid fractions. The gas phase in the autoclave was analyzed using a gas chromatograph.

2. Results and discussion

The current results have mainly involved the proton- lignosulfonate (H-LS) sample, while results for other lignins are underway. The results (Presented in Table 1.) show that the conversion of H-LS increased significantly by the presence of NiMo catalyst; while an oil yield of 24 wt% (Exp. No. 1) was observed in a non-catalytic test, the oil yield increased to 62 wt% (Exp. No. 2) over NiMo catalyst. According to the GC-MS analysis, methyl substituted phenols are among the products in the oil fractions. It is assumed that by thermal cleavage of C-O-C and C-C bonds in the structure of lignin, monomers and oligomers are formed in the reaction medium. The higher bio-oil yield over NiMo catalyst is possibly resulting from catalytic cleavage of ether bonds[2] and potentially also suppression of repolymerization reactions involving reaction of in-situ degraded compounds over catalytic active sites. The carbon to oxygen ratio (C/O) is an indicator of

the quality and stability of the bio-oil. The C/O ratio of H-LS is 1.9, which increased from 2 in non-catalytic conversion to 2.6 in NiMo catalyzed conversion of H-LS.

The reusability of the NiMo catalyst from conversion of H-LS was also investigated: Conversion of H-LS with a used catalyst without any pretreatment resulted in an oil yield of 61 wt% (Exp. No. 3). The two times used catalyst was further used for conversion of H-LS at 305 ˚C (Exp. No. 4), which resulted in an oil yield of 57 wt%. It can be concluded that the catalyst from conversion of H-LS is usable at least three times without a major decline in obtained oil yield.

No effect was observed by presulfidation of NiMo catalyst for conversion of H-LS, which contains 3 wt% sulfur. Conversion of H-LS with catalyst: lignin: solvent ratio of 0.5 g: 5 g: 50 ml at 310 ˚C on presulfided and non-presulfided NiMo catalyst resulted in 71 (Exp. No. 5) and 72 wt% (Exp. No. 6) of oil yields, respectively. It is speculated that simultaneous activation of the catalyst occurs during conversion of H-LS by thermal cleavage of C-S bonds in the lignin, which may be followed by successive adsorption of sulfur/ sulfonate compounds on the catalyst's active phase.

Table 1. Experiments conditions for conversion of H-LS with initial hydrogen loading of 25 barg and 3 hours reaction time.

Exp. No.	Catalyst	Reaction T [˚C]	Catalyst: Lignin: Solvent	Oil yield wt%
1	Non- catalytic	310	0 g: 10 g: 100 ml	24
2	NiMo (Non-presulfided)	310	1 g: 10 g: 100 ml	62
3	NiMo (Non-presulfided, used once, included char)	310	1 g: 10 g: 100 ml	61
4	NiMo (Non-presulfided, used twice, included char)	305	1 g: 10 g: 100 ml	57
5	NiMo (Presulfided)	310	0.5 g: 5 g: 50 ml	71
6	NiMo (Non-presulfided)	310	0.5 g: 5 g: 50 ml	72

3. Conclusions

A solvothermal method using a NiMo sulfide catalyst is introduced for conversion of different types of lignin. A positive impact is observed by addition of the NiMo catalyst to the reaction medium as the oil yield thereby increased from 24 wt% in the absence of the catalyst to 62 wt% in the presence of the NiMo catalyst. The reaction products can either be used as heavy fuel oil or can further be tailored towards the desired products by subsequent treatment methods such as desulfurization and deoxygenation.

References

1. A. Narani, R.K. Chowdari, C. Cannilla, G. Bonura, F. Frusteri, H.J. Heeres, K. Barta, *Green Chem*. **2015**, *17*, 5046-5057
2. C.R. Kumar, N. Anand, A. Kloekhorst, C. Cannilla, G. Bonura, F. Frusteri, K. Barta, H.J. Heeres, *Green Chem*. **2015**, *17*, 4921-4930.